Pulsed-DC Reactive Magnetron Sputtering of Vanadium Dioxide Thermochromic Thin Films

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Abstract

Vanadium oxides are an important class of materials with a large diversity of physical and chemical properties which derive from a range of single or mixed valences and a large variety of structures. They are already being used in many technological applications such as electrical and optical switching devices, light detectors, temperature sensors, etc. There has been a great interest in a particular phase, VO_2(M), due to its thermochromic behaviour near room temperature which allows the development of smart windows with active control of the solar spectrum, for energy efficiency purposes. However, stoichiometric VO_2 is difficult to deposit because of a narrow stability range due to the complex vanadium-oxygen reactive system.

In this work, vanadium oxide thin films were synthesised on glass substrates by reactive pulsed-dc magnetron sputtering from a vanadium metal target in a O_2/Ar atmosphere. Different processing conditions have been chosen in order to evaluate their influence on the crystal phases formed, surface morphologies and thicknesses and optical performance. The films were characterized by X-ray diffractometry (XRD) in order to examine the crystal structure and identify the phases present in the different films. The obtained VO_2(M) films

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were thereafter analysed in terms of surface morphology by scanning electron microscopy (SEM) and the characteristic reversible semiconductor-metal transition of the VO_2 films was evaluate by optical spectrophotometry in the UV-Vis-NIR.

Keywords: Pulsed-DC sputtering; VO2; Thermochromic films; IR modulation; Optical switches

1. Introduction

Reactive DC sputtering from a metal target is a very complex process. When depositing a film it is expected that the reactive gas combines with the sputtered metal to form the desirable compound on the surface of substrate. However, adversely the reactive gas also reacts with the target material, chamber walls and fixturings. The reaction on the target surface also leads to formation of compound, the so-called target poisoning effect. The compound formed at the target surface is typically less conductive than the target metal or even insulating. This will result in positive charge build-up resulting from the bombarding ions. Arcing may occur if the charge reaches the breakdown voltage for the insulating film and the consequence could be droplets being ejected from the target surface towards the growing film which in turn degrade the film quality [1, 2]. To overcome these typical problems of the reactive sputtering process, radio-frequency (RF) or pulsed DC power supplies were introduced. RF power supplies are more expensive than the DC ones and require a complex system [2]. Moreover, the deposition rate with RF power is very low, about half the rate for DC power, for an equivalent amount of power [2, 3]. Asymmetric-bipolar pulsed DC sputtering is ideal to reactively deposit oxides and nitrides from metallic targets since during the process, the polarity of the target voltage is periodically reversed from

negative to positive [4, 5]. In this context asymmetric simply means that the reverse positive pulse height is lower than that of the negative one but high enough to neutralise charge build-up on the target surface.

Usually, when reactively sputtering oxides such as Al_2O_3 or SiO_2, the problem commonly reported concerns to deposition rates which are considerably low compared to those of the metal elements, for the same power. However, when depositing complex systems such as vanadium oxides with several oxidation states and polymorphs [6], the instability of the process may be detrimental to the synthesis of a specific single phase film. Among all vanadium oxides, VO_2 has attracted a high interest due to its thermochromism evidenced by reversely switching its reflectivity to IR light with temperature, near room temperature. Although there are many publications reporting on VO_2 films prepared by reactive sputtering, there is not enough knowledge on the ideal conditions to grow the thermochromic VO_2(M) phase. In this work, due to the typical reactive sputtering process instability, a preliminary study was done by varying the cathode current intensity, at a given O_2/Ar ratio, as a mean to examine the boundaries of the metal and compound sputtering modes for a vanadium target. A first set of films was prepared with different current intensities with the purpose of preparing film with different vanadium/oxygen contents. A second set of films was prepared at a cathode current found to give rise to the desirable film stoichiometry and structure, monoclinic VO_2 phase. For this set, different deposition times were chose envisaging distinct film thicknesses. The prepared films were structurally characterized by XRD and those containing VO_2 were thereafter examined by SEM and their optical/thermochromic performance evaluated by spectrofotometry.

2. Experimental details

The preparation of the vanadium oxide films was carried out by asymmetric-bipolar pulsed-DC (Advanced Energy 5kW Pinnacle Plus+ power supply) magnetron sputtering from a high purity (99.95%) metallic vanadium target in a oxygen/argon reactive atmosphere. SiO_2-coated float glass pieces were used as substrates. The first set of films was prepared with different current intensities, which corresponded to different positions along the voltage curve in Fig. 1, when decreasing current. A second set of films was prepared at a cathode current found to give rise to the desirable film stoichiometry and structure, monoclinic VO_2 phase. For this set, different deposition times were chose envisaging distinct film thicknesses. The main process parameters used to synthesize the vanadium oxide films are shown in Table 1.

X-ray diffractometry (XRD) analysis has been carried out on the various films with the purpose of examining the crystal structure and to identify the vanadium oxide phases formed under the different processing conditions. The diffractometer was operated with a continuous scan of Cu Kα1 radiation with λ=1.54056Å. Scanning electron microscopy (SEM) was used to examine the morphology characteristics and to estimate the thicknesses of the VO_2 films. The optical/thermochromic behaviour of the VO_2 films has been evaluated in an optical spectrophotometer with an embedded sample heating-cooling cell. It has been done by measuring the spectral normal transmittance at the UV-VIS-NIR range, from 250 to 2500 nm, in both semiconducting and metallic states.

3. Results and discussion

3.1. Analysis of the reactive sputtering process

In Fig. 1 is plotted the cathode voltage change versus the imposed cathode current, during decrease followed by increase. It can be observed a typical example of the voltage change in a reactive sputtering process. As the cathode current is decreased, the compound layer starts to form on the target surface and due to its resistivity being higher than that of the pure metallic target the power supply raises the voltage in order to keep the imposed current. This dynamic behaviour can also be observed at a constant current and varying the O_2/Ar flow ratio. The cathode reactions are seen to increase suddenly at some point, due to development of the target compound layer and positive charge build-up, and consequently a drastic change in the growing film stoichiometry, from metal-rich to gas-rich (as shown in section 3.2) due to complete target “poisoning” is observed. When decreasing the current, an opposite behaviour is observed although the discharge voltage does not follow the same line presenting a hysteresis effect. This hysteresis is a consequence of two competitive processes: the sputtering of the target surface and the covering of its surface by reaction products [7]. The nature of the hysteresis effect is addressed and explained in detail in a review paper by Safi [8].

3.2. Structural characterization of the films

In Fig. 2 are shown XRD patterns of films deposited with different current intensities corresponding to different starting cathode voltages according to the hysteresis curve (when decreasing current, going from metal mode to compound mode) illustrated in Fig. 1. It can be observed that the change in current intensity allows the growing of films with different

oxidation states as a consequence of the poisoning level of the target. The optimum current intensity range which allows the formation of VO_2 is very narrow and is located right at the onset of the transition (position 1 in Fig. 1) from metal to compound regime of the sputtering target composition. At this point, the voltage change with time was subtle showing a maximum increase of about 2V per minute which allowed the growth of single phase stoichiometric VO_2, as seen on patterns (c-e). The only peak at $2\theta=39.7^{o}$ is indexed to the (002) plane reflection of the monoclinic VO_2(M) phase [9]. It was noticeable to the naked eye the darkening of the brown color and loss of transparency of the VO_2 films with the increase of cathode current. This is a consequence of the higher sputtering yield of vanadium due to higher cathode current which results in higher deposition rates and formation of oxides with decreasing oxygen contents. For currents higher than 0.59A (to the right of point 1 in Fig. 1) the XRD results, seen on patterns (a-b), indicate formation substoichiometric oxides. The film grown at a cathode current of 0.6A shows only a peak centred at $2\theta=39.3^{o}$ which could be interpreted as a shifting of the (002) plane reflection peak of the VO_2(M) phase to lower angles. Moreover, it is also noticeable a broadening of the peak which together with the shifting indicate abundant presence of lattice defects resulting from different types of internal stresses and planar faults, especially stacking faults or twin boundaries [10]. To the naked eye this film is black and completely opaque to light. The pattern in Fig. 2(a) has not been indexed no any specific vanadium oxide phase but the plane reflection peaks are very close to those of VOx where x is in the range of 0.5 to 1. Within the transition region, when going to lower current values, (between positions 1 and 2 in Fig. 1) the process is very unstable, i.e. the cathode voltage immediately increases to voltage values over 420V and then remain approximately constant, indicating a fully oxidation of the target cathode. Due to the high process instability in this region it was not possible to deposit any film. We have also prepared films in the compound mode (to the left of position 2 in Fig. 1) for currents of 0.52A

and 0.48A which in this case allowed the formation of overstoichiometric films containing multiple vanadium oxide phases such as V_2O_5, β-V_2O_5 and V_6O_{13}, as seen in patterns (f) and (g).

A second set of films has subsequently been prepared and taking into account the XRD results (Fig. 2) achieved previously a cathode current of 0.58A has been chosen for deposition of VO_2 films with different thicknesses. The XRD patterns for this set of films are presented in Fig. 3. It can be observed in patterns (a) and (b) taken from films deposited for 3 and 4 minutes, respectively, single phase VO_2(M) with preferred crystal orientation along the (002) plane direction at $2\theta=39.7^{o}$, although some traces of crystallites oriented along (011) are noticeable at $2\theta=27.8^{o}$. Pattern (c) was obtained in a film prepared by depositing 4 subsequent layers of 3 minutes each. Again, solely VO_2(M) phase has been detected in the film although the peak intensities raised due to the higher crystalline volume involved in the XRD analysis. Moreover, peak FWHM of (002) oriented crystallites decreased indicating an increase of crystallite sizes. Pattern (d) corresponds to a film grown for 30 minutes and as it can be observed several VOx phases were formed during film growth, VO_2(M), V_3O_7, V_2O_5, β-V_2O_5. For long deposition times, even in conditions where instability of the reactive process is reduced, due to the continuous increase of oxide layer formed at the target surface (as realized by the slight target voltage increase during deposition), there will be a change in the sputtering yield of vanadium and consequently a tendency for formation of overstoichiometric oxides. At the beginning of the deposition until at least the first 4 minutes VO_2(M) is formed as seen in pattern (b). However, at some point of the deposition, vanadium oxide phases with higher oxygen valences will start to nucleate and grow, which in this processing conditions, V_3O_7, V_2O_5, β-V_2O_5 were given rise. A multistep film growth is a way of overcoming this situation, as observed in the film grown in 4 layers of 3 minutes each, in pattern (c). The

instability of the reactive sputtering process is an issue of major concern and to date there have been reported several approaches to overcome it [2].

3.3. Film morphology and thickness

In Fig. 4 is presented the surface morphology of the VO_2 film prepared with the lowest deposition time, 3 minutes and fracture views of the microstructures of the films with different thicknesses. As shown in Fig. 4(a) the film morphology is characterized typically by a matrix of spherical-like grains with embedded elongated grains up to about 350 nm long, lying on the film plane. The cross-sectional fracture view of the films depicted in Fig. 4(b-f) show the microstructure of the films grown for different deposition times and allows estimating the respective film thicknesses. The films are found to be very dense and uniform and do not enclose the columnar microstructure very common in sputtered films.

In Fig. 5 is plotted the relationship between the various film thicknesses and the respective deposition times. Within the time range of the deposited films it can be observed a linear behaviour which indicates a constant deposition rate of about 15nm/min. For lower deposition times the deposition rate is obviously higher and is due to a higher sputtering yield which results from a less oxidized target at the beginning of the deposition process. Moreover, it is most probable that the films are highly disordered or amorphous at the beginning of nucleation and growth process due to the amorphous glass substrate which could result in a poorly dense film within a certain thickness range.

3.4. Optical performance

Fig. 6 compares the optical transmittance spectra of the VO_2 films deposited for 3, 12 and 30 minutes from the UV to the NIR wavelength range, on both the semiconducting (15ºC) and metallic (85ºC) states. As it can be observed all films reveal the semiconductor-metal phase transition typical of VO_2 which is characterized by an optical switch of the response to IR light. This transition takes place at around 68ºC and is a result of a first-order structural transition going from a monoclinic to a tetragonal structure on heating [11, 12]. The optical switching at NIR is very marked for all films whereas no significant change at the visible range is observed. The film thickness clearly affects the luminous transmittance as seen by the maximum at around 40% and 13%, for 135 (3min.) and 270nm (12min.), respectively. The film deposited for 30min, which is 550nm thick, presents higher luminous transmittance than that of the film deposited for 12min. as a consequence of comprising not only VO_2 but also V_2O_5, having the latter better luminous transparency. It seems that the V_2O_5 did not affect the IR modulation efficiency of VO_2 in the film.

4. Conclusions

In this work we report on the conditions to successfully grow VO_2 thermochromic thin films. We have prepared several films for a constant O_2/Ar flow ratio and varied the discharge current in order to sputter from different target poisoning levels. The structural analyses have shown diverse vanadium oxidation states as a consequence of different sputtering yields resulting from the different target poisoning levels. The obtained VO_2 films are found to be very dense and uniform and do not enclose the columnar microstructure very common in sputtered films. All films revealed a marked IR modulation when going through the

semiconductor-metal transition. The thickness of the VO_2 film has a clear influence on the luminous transmittance.

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Table 1. Main processing parameters for deposition of VO_2 films

Base pressure (mbar)	$3x10^{-5}$
Work pressure (mbar)	$1x10^{-3}$
Oxygen/Argon ratio (%)	50
Total gas flow (sccm)	6
DC current (A)	Variable
Deposition time (min.)	Variable
Pulse frequency (kHz)	10
Reverse time (μs)	5
Target-subst. dist. (mm)	48
Target diameter (mm)	75
Substrate temperature (ºC)	460

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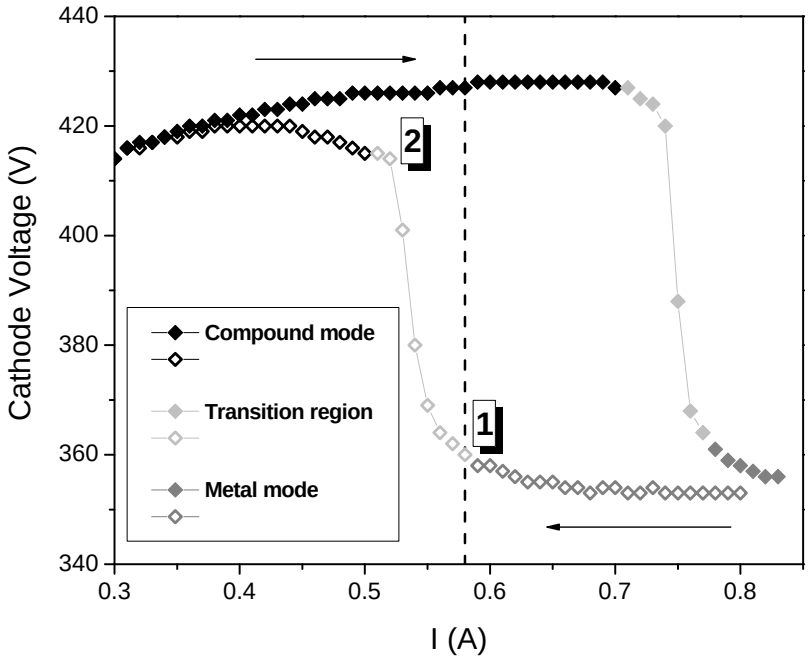

Fig. 1. Variation of cathode voltage as a function of cathode current intensity at a total pressure P = 1.0e^{-3}mbar and a reactive/sputter gas fraction O_2/Ar = 0.5. Solid/hollow symbols = increase/decrease of current respectively.

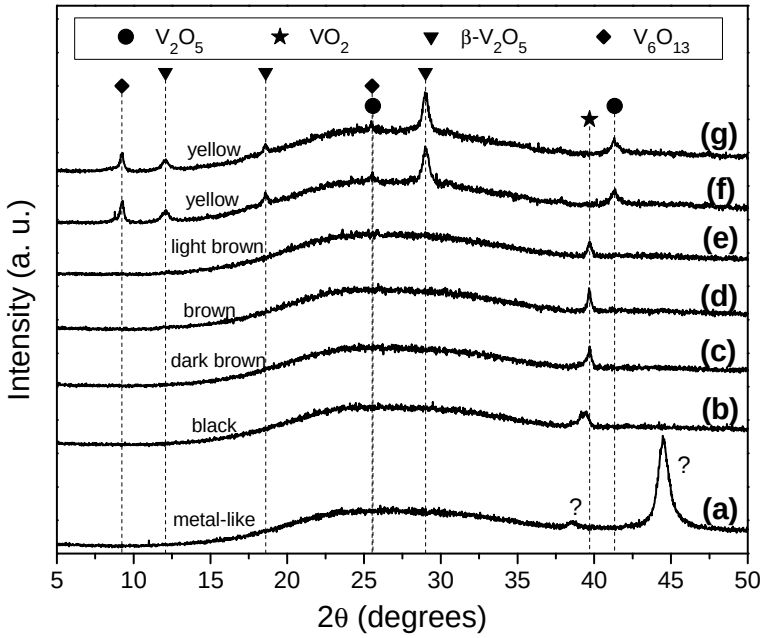

Fig. 2. XRD patterns of the vanadium oxide films deposited for 4 minutes with different cathode current intensities: (a) I=0.70A; (b) I=0.60A; (c) I=0.59A; (d) I=0.58A; (e) I=0.55A; (f) I=0.52A; (g) I= 0.48A

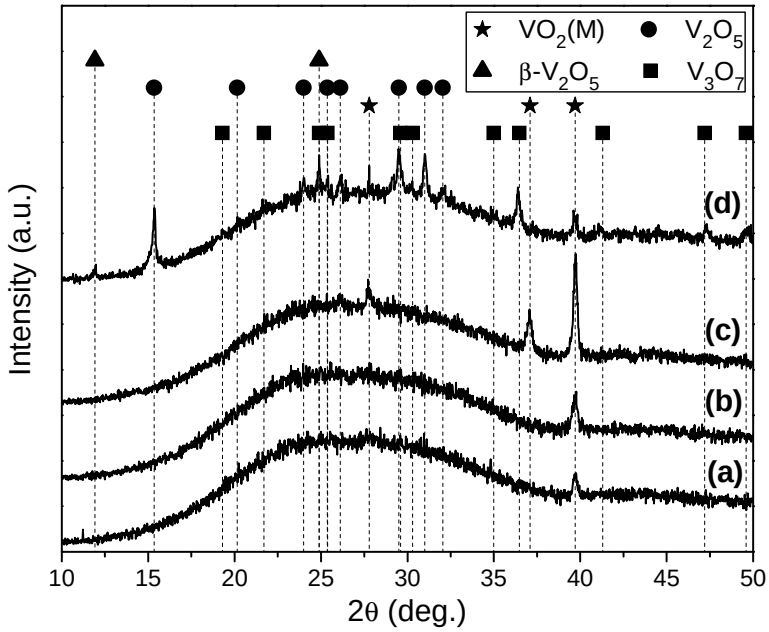

Fig. 3. XRD patterns of vanadium oxide films prepared with I=0.58A and different deposition times: (a) 3 min.; (b) 4 min; (c) 12 min (4 layers of 3min); (d) 30 min.

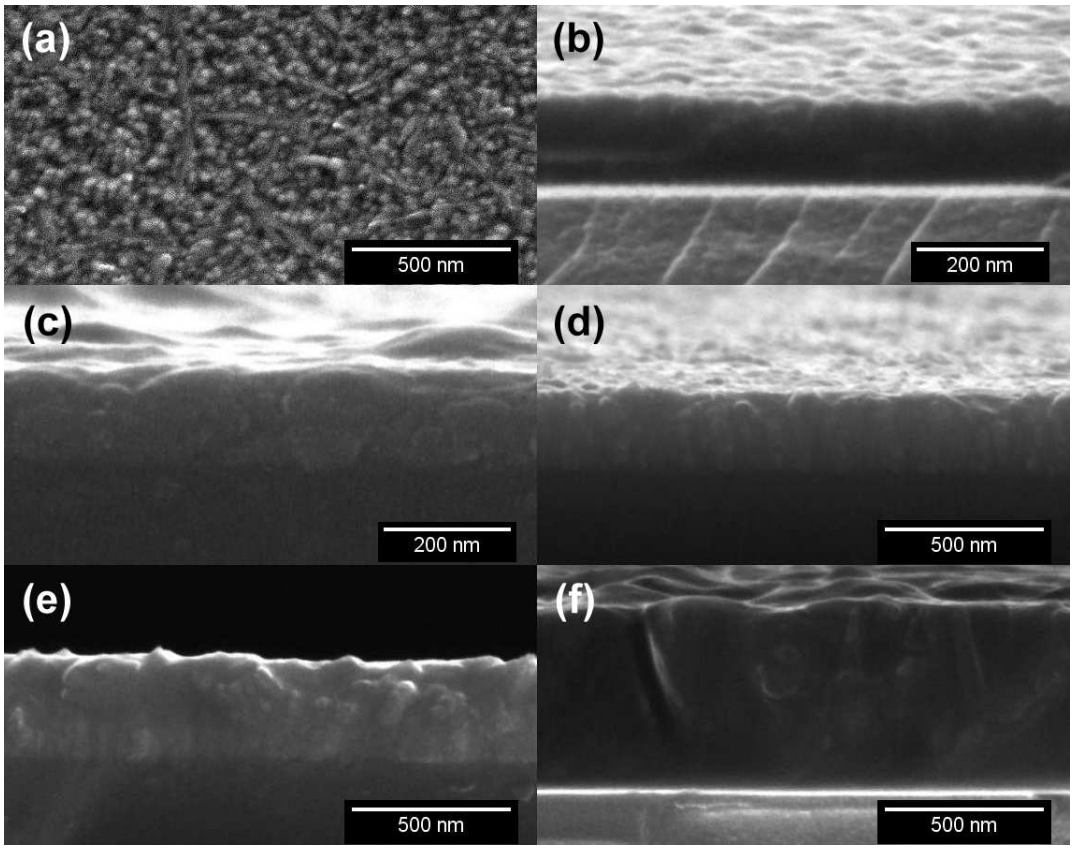

Fig. 4. SEM micrograph of the surface of the VO_2 film grown for 3 min (a) and SEM cross-sectional fracture view of the microstructures of the films grown for 3, 4, 12, 16 and 30 minutes, respectively (b-f).

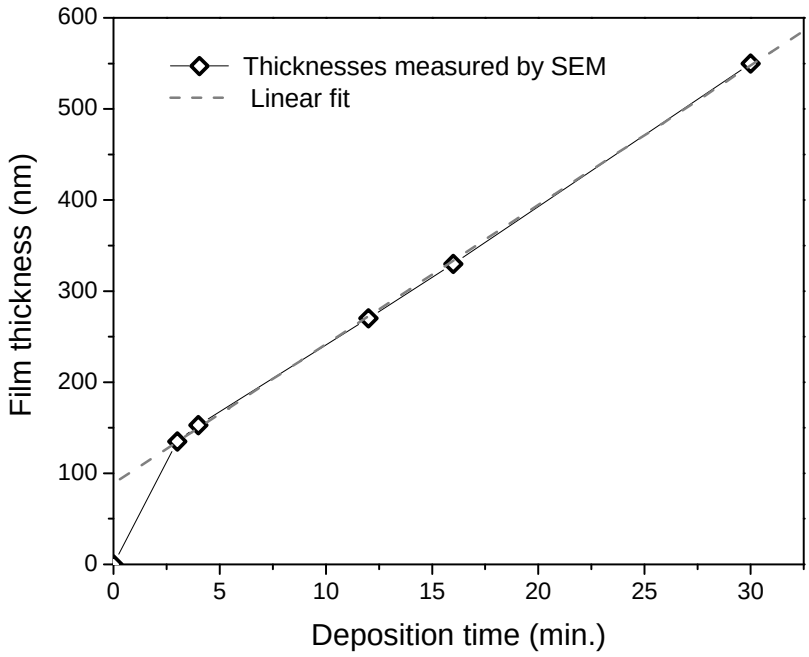

Fig. 5. Relationship between the obtained film thicknesses (measured by SEM) and the deposition time.

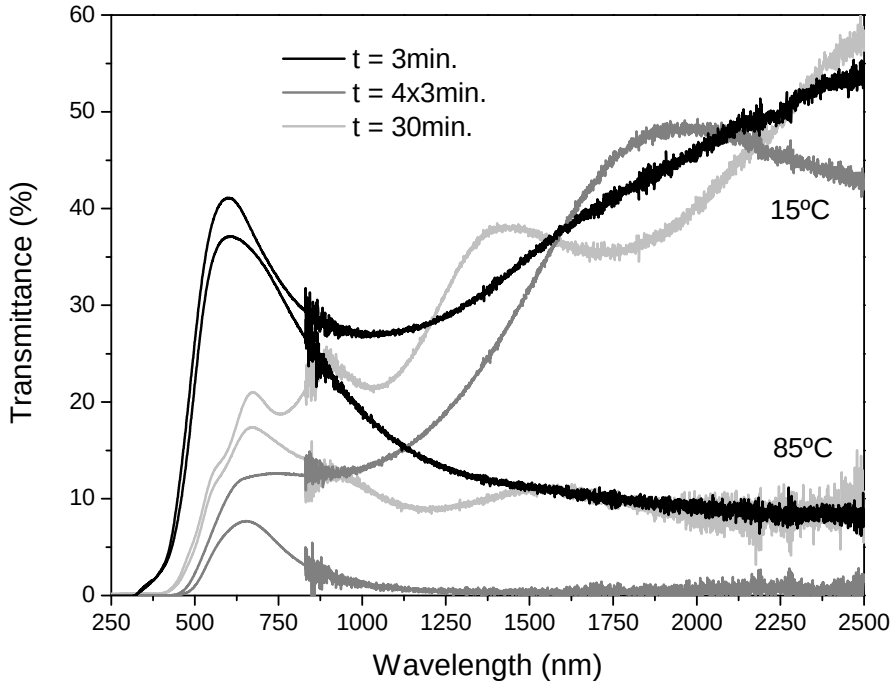

Fig. 6. Optical transmittance of VO_2 films as a function of wavelength in the UV-Vis-NIR on both semiconducting and metallic states.